PHYSICAL REVIEW B VOLUME 9, NUMBER 4 15 FEBRUARY 1974

Relationship between two-body interatomic potentials in a lattice model and elastic constants. II[†]

R. A. Johnson

Department of Materials Science, University of Virginia, Charlottesville, Virginia 22901

(Received 30 July 1973)

General equations are derived for the second-, third-, and fourth-order elastic constants given by a lattice model for a monatomic material, based on two-body central interactions and volume-dependent energy contributions. Explicit equations for a cubic lattice are given. The Brugger definition of the elastic constants is used with the required expansions in terms of the Lagrangian strain parameter. The relationship between the two-body and volume-dependent terms arising from the condition of equilibrium at zero initial stress is discussed in detail.

I. THEORY

It was shown in an earlier paper,[1] referred to as I, that the bond energy per unit undeformed volume for a monatomic crystal can be expanded in powers of strain parameters α_{ij} for a homogeneous deformation as

$$E_b = A + \alpha_{ij}A_{ij} + \tfrac{1}{2}\alpha_{ij}\alpha_{kl}A_{ijkl} + \cdots \ , \qquad (1)$$

where

$$\alpha_{ij} = \frac{\partial u_j}{\partial a_i} \ ,$$

$$A = \frac{1}{2\Omega_0}\sum_s \phi(\vec{\mathrm{r}}^s)\big|_0 \ ,$$

$$A_{ij} = \frac{1}{2\Omega_0}\sum_s \frac{\partial\phi(\vec{\mathrm{r}}^s)}{\partial r_j^s}\bigg|_0 a_i^s \ ,$$

$$A_{ijkl} = \frac{1}{2\Omega_0}\sum_s \frac{\partial^2\phi(\vec{\mathrm{r}}^s)}{\partial r_j^s \partial r_l^s}\bigg|_0 a_i^s a_k^s \ , \text{ etc.},$$

with Ω_0 the undeformed atomic volume, $\phi(\vec{\mathrm{r}}^s)$ the potential energy function for two atoms separated by the vector $\vec{\mathrm{r}}^s$, the sum is taken over the position vectors of all lattice atoms relative to an atom at the origin, r_j^s is a Cartesian component of $\vec{\mathrm{r}}^s$, $\vec{\mathrm{a}}^s$ is the undeformed value of $\vec{\mathrm{r}}^s$, $\vec{\mathrm{u}}^s = \vec{\mathrm{r}}^s - \vec{\mathrm{a}}^s$ is the displacement vector, evaluation of the derivatives are at the undeformed state, and the summation implied is by repeated indices.

If $\phi(\vec{\mathrm{r}}^s)$ is a central potential $\phi(\vec{\mathrm{r}}^s) = \phi(r^s) \equiv \phi_s$, the expansion can be transformed to

$$E_b = B + \eta_{ij}B_{ij} + \tfrac{1}{2}\eta_{ij}\eta_{kl}B_{ijkl} + \cdots \ , \qquad (2)$$

with η_{ij} the Lagrangian strain parameter $\eta_{ij} = \frac{1}{2}(\alpha_{ij} + \alpha_{ji} + \alpha_{ik}\alpha_{jk})$ (the symmetric finite-strain parameter introduced by Murnaghan[2]) and

$$B = \frac{1}{2\Omega_0}\sum_s \phi_s\big|_0 \ ,$$

$$B_{ij} = \frac{1}{2\Omega_0}\sum_s \left(\frac{1}{r^s}\frac{\partial\phi_s}{\partial r^s}\right|_0 a_i^s a_j^s \ ,$$

$$B_{ijkl} = \frac{1}{2\Omega_0}\sum_s \left(\frac{1}{r^s}\frac{\partial}{\partial r^s}\frac{1}{r^s}\frac{\partial\phi_s}{\partial r^s}\right|_0 a_i^s a_j^s a_k^s a_l^s \ , \text{ etc.}$$

With the definition of the elastic constants as given by Brugger[3] and discussed by Wallace,[4]

$$C_{ij} = \frac{\partial U}{\partial\eta_{ij}} \ ,$$

$$C_{ijkl} = \frac{\partial^2 U}{\partial\eta_{ij}\,\partial\eta_{kl}} \ , \text{ etc.},$$

where U is the internal energy per unit undeformed volume, the change in internal energy is given by

$$\Delta U = \eta_{ij}C_{ij} + \tfrac{1}{2}\eta_{ij}\eta_{kl}C_{ijkl} + \cdots \ , \qquad (3)$$

with the elastic constants evaluated at the state of zero strain. Direct comparison of Eqs. (2) and (3) gives

$$C_{ij\cdots} = B_{ij\cdots} \ . \qquad (4)$$

If the initial state from which measurements are taken is assumed to be stress free, then C_{ij} is zero and the potential and lattice symmetry must be such that $B_{ij} = 0$. In general, the restriction on the potential from this condition is sufficiently severe that the experimental second-order elastic constants cannot be matched by Eq. (4). To circumvent this problem, an additional strain term $E_s = -\eta_{ij}B_{ij}$ can be added to the change in bond energy for a lattice-model calculation. With this scheme, an over-all η_{ij} strain associated with a defect configuration would have to be determined and E_s added to the energy associated with changes in bond lengths to calculate a defect energy.

The strain η_{ij} is difficult to determine in a defect calculation, whereas the volume change is easily found. Thus, lattice models have been used with an energy contribution which is solely a function of the volume change for the additional term required to maintain equilibrium in the unstressed state. Although this procedure is not as general as the method outlined in the previous paragraph, it has been found to be satisfactory for most cases. Brudnoy[5] has recently determined a potential for hcp zirconium using the strain method. The mathematical requirement for equilibrium to be attained by volume-dependent forces at zero initial stress is that the potential and lattice structure be such that $A_{ij} = K\delta_{ij}$. If this condition does not hold, a term E_s must be added to the model energy.

II. ELASTIC CONSTANTS FOR A CENTRAL POTENTIAL AND VOLUME-DEPENDENT TERMS

Since there has been some confusion in regard to the expansion of the volume in strain parameters, V/V_0 is listed for expansion in terms of $\beta_{ij} = \alpha_{ij} + \delta_{ij}$, α_{ij}, and η_{ij}:

$$V/V_0 = \tfrac{1}{6}(\beta_{ii}\beta_{jj}\beta_{kk} - 3\beta_{ii}\beta_{jk}\beta_{kj} + 2\beta_{ij}\beta_{jk}\beta_{ki}) , \tag{5a}$$

$$V/V_0 = 1 + \alpha_{ii} + \tfrac{1}{2}(\alpha_{ii}\alpha_{jj} - \alpha_{ij}\alpha_{ji}) + \tfrac{1}{6}(\alpha_{ii}\alpha_{jj}\alpha_{kk} - 3\alpha_{ii}\alpha_{jk}\alpha_{kj} + 2\alpha_{ij}\alpha_{jk}\alpha_{ki}) , \tag{5b}$$

$$V/V_0 = [1 + 2\eta_{ii} + 2(\eta_{ii}\eta_{jj} - \eta_{ij}\eta_{ji}) + \tfrac{4}{3}(\eta_{ii}\eta_{jj}\eta_{kk} - 3\eta_{ii}\eta_{jk}\eta_{kj} + 2\eta_{ij}\eta_{jk}\eta_{ki})]^{1/2} . \tag{5c}$$

Then, to fourth order in η,

$$\begin{aligned}(V/V_0)^n = {} & 1 + n\eta_{ii} + \tfrac{1}{2}n(n\eta_{ii}\eta_{jj} - 2\eta_{ij}\eta_{ji}) + \tfrac{1}{6}n(n^2\eta_{ii}\eta_{jj}\eta_{kk} - 6n\eta_{ii}\eta_{jk}\eta_{kj} + 8\eta_{ij}\eta_{jk}\eta_{ki}) \\ & + \tfrac{1}{24}n(n-2)[(n^2+2n+8)\eta_{ii}\eta_{jj}\eta_{kk}\eta_{ll} - 12(n+2)\eta_{ii}\eta_{jj}\eta_{kl}\eta_{lk} + 32\eta_{ii}\eta_{jk}\eta_{kl}\eta_{lj} + 12\eta_{ij}\eta_{ji}\eta_{kl}\eta_{lk}] .\end{aligned} \tag{6}$$

To relate the model-energy change $\Delta E_b + \Delta E_v$ [where $E_v = P(V/V_0)^n$] to the elastic energy given by Eq. (3), the symmetry properties of the elastic constants must be considered. As pointed out in I, this is because the energy change involves summations and does not lead directly to unique correspondence of terms with respect to subscripts. With elastic-constant symmetry taken into account,

$$C_{ij} = B_{ij} + nP\Delta_{ij} , \tag{7a}$$

$$C_{ijkl} = B_{ijkl} + n^2P\Delta_{ijkl} - nP\Delta_{ijkl} , \tag{7b}$$

$$C_{ijklmn} = B_{ijklmn} + n^3P\Delta_{ijklmn} - n^2P\Delta_{ijkmln} + nP\Delta_{ikjmln} , \tag{7c}$$

$$\begin{aligned}C_{ijklmnpq} = {} & B_{ijklmnpq} + n(n-2)(n^2+2n+4)P\Delta_{ijklmnpq} - n(n-2)(n+2)P\Delta_{ijklmpnq} \\ & + n(n-2)P\Delta_{ijkmlpnq} + n(n-2)P\Delta_{ikjlmpnq} .\end{aligned} \tag{7d}$$

The symbol $\Delta_{abcdef}\ldots$ means the sum of all independent arrangements of the term $\delta_{ab}\delta_{cd}\delta_{ef}\ldots$ from interchange of i and j, k and l, m and n, $\cdots$ and interchange of ij with kl, ij with mn, kl with mn, $\cdots$. Thus, for example

$$\Delta_{ij} = \delta_{ij} ,$$

$$\Delta_{ikjl} = \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} ,$$

$$\Delta_{ijkmln} = \delta_{ij}\delta_{km}\delta_{ln} + \delta_{ij}\delta_{kn}\delta_{lm} + \delta_{kl}\delta_{im}\delta_{jn} + \delta_{kl}\delta_{in}\delta_{jm} + \delta_{mn}\delta_{ik}\delta_{jl} + \delta_{mn}\delta_{il}\delta_{jk} .$$

The number of terms associated with each Δ is: Δ_{ij}, Δ_{ijkl}, Δ_{ijklmn}, $\Delta_{ijklmnpq}$, 1; Δ_{ikjl}, 2; Δ_{ijkmln}, 6; Δ_{ikjmln}, 8; $\Delta_{ijklmpnq}$, $\Delta_{ikjlmpnq}$, 12; and $\Delta_{ijkmlpnq}$, 32. As pointed out in I, these equations can be extended to the case of several different volume-dependent terms by simply summing their contributions. For example, with two contributions, Eq. (7a) becomes

$$C_{ij} = B_{ij} + (n_1P_1 + n_2P_2)\Delta_{ij} .$$

III. CUBIC SYMMETRY

For cubic symmetry in a monatomic lattice, with Voigt notation (11 → 1, 22 → 2, 33 → 3, 23 → 4, 31 → 5, 12 → 6), Eq. (7) reduces to

$$C_1 = \frac{1}{2\Omega_0}\sum_s \psi_s'(x^s)^2 + nP , \tag{8a}$$

$$C_{11} = \frac{1}{2\Omega_0}\sum_s \psi_s''(x^s)^4 + n(n-2)P , \tag{8b}$$

$$C_{12} = \frac{1}{2\Omega_0}\sum_s \psi_s''(x^s)^2(y^s)^2 + n^2P , \tag{8c}$$

$$C_{44} = \frac{1}{2\Omega_0}\sum_s \psi_s''(x^s)^2(y^s)^2 - nP , \tag{8d}$$

$$C_{111} = \frac{1}{2\Omega_0}\sum_s \psi_s'''(x^s)^6 + n(n-2)(n-4)P , \tag{8e}$$

$$C_{112} = \frac{1}{2\Omega_0}\sum_s \psi_s'''(x^s)^4(y^s)^2 + n^2(n-2)P , \tag{8f}$$

$$C_{166} = \frac{1}{2\Omega_0}\sum_s \psi_s'''(x^s)^4(y^s)^2 - n(n-2)P , \tag{8g}$$

$$C_{144} = \frac{1}{2\Omega_0}\sum_s \psi_s'''(x^s)^2(y^s)^2(z^s)^2 - n^2P , \tag{8h}$$

$$C_{123}=\frac{1}{2\Omega_0}\sum_s \psi_s'''(x^s)^2(y^s)^2(z^s)^2+n^3P\ , \qquad (8i)$$

$$C_{456}=\frac{1}{2\Omega_0}\sum_s \psi_s'''(x^s)^2(y^s)^2(z^s)^2+nP\ , \qquad (8j)$$

$$C_{1111}=\frac{1}{2\Omega_0}\sum_s \psi_s''''(x^s)^8+n(n-2)(n-4)(n-6)P\ , \qquad (8k)$$

$$C_{1112}=\frac{1}{2\Omega_0}\sum_s \psi_s''''(x^s)^6(y^s)^2+n^2(n-2)(n-4)P\ , \qquad (8l)$$

$$C_{1166}=\frac{1}{2\Omega_0}\sum_s \psi_s''''(x^s)^6(y^s)^2-n(n-2)(n-4)P, \qquad (8m)$$

$$C_{1122}=\frac{1}{2\Omega_0}\sum_s \psi_s''''(x^s)^4(y^s)^4+n^2(n-2)^2P, \qquad (8n)$$

$$C_{1266}=\frac{1}{2\Omega_0}\sum_s \psi_s''''(x^s)^4(y^s)^4-n(n-2)^2P, \qquad (8o)$$

$$C_{6666}=\frac{1}{2\Omega_0}\sum_s \psi_s''''(x^s)^4(y^s)^4+3n(n-2)P, \qquad (8p)$$

$$C_{1123}=\frac{1}{2\Omega_0}\sum_s \psi_s''''(x^s)^4(y^s)^2(z^s)^2+n^3(n-2)P, \qquad (8q)$$

$$C_{1144}=\frac{1}{2\Omega_0}\sum_s \psi_s''''(x^s)^4(y^s)^2(z^s)^2-n^2(n-2)P, \qquad (8r)$$

$$C_{5566}=\frac{1}{2\Omega_0}\sum_s \psi_s''''(x^s)^4(y^s)^2(z^s)^2+n(n-2)P, \qquad (8s)$$

$$C_{1255}=\frac{1}{2\Omega_0}\sum_s \psi_s''''(x^s)^4(y^s)^2(z^s)^2-n^2(n-2)P, \qquad (8t)$$

$$C_{1456}=\frac{1}{2\Omega_0}\sum_s \psi_s''''(x^s)^4(y^s)^2(z^s)^2+n(n-2)P\ . \qquad (8u)$$

The notation

$$\psi_s'=\frac{1}{r^s}\frac{\partial\phi_s}{\partial r^s}\bigg|_0,\quad \psi_s''=\frac{1}{r^s}\frac{\partial}{\partial r^s}\frac{1}{r^s}\frac{\partial\phi_s}{\partial r^s}\bigg|_0,\ \ldots$$

has been used. Standard cubic relations, e.g., $C_{11}=C_{22}=C_{33}$, $C_{112}=C_{223}$, ..., are implied in this listing. Two relationships for the fourth-order elastic constants are found with this model which are not required by normal elastic-constant symmetry: $C_{1144}=C_{1255}$ and $C_{5566}=C_{1456}$ (in full notation $C_{11112323}=C_{11221313}$ and $C_{12121313}=C_{11233112}$).

IV. DISCUSSION

Thomas[6] has recently carried out a pseudopotential calculation of the third-order elastic constants of copper and silver, and reports that the overlap energy (approximated by a Born-Mayer central force) makes the dominant contribution to the third-order constants. A fitting with a nearest-neighbor two-body central force and a single volume-dependent term using the above formalism gives very similar results (see Appendix). It is felt that, in some respects, the discussion given by Thomas may be misinterpreted. He lists the contributions from four terms separately: band structure, free electron, electrostatic, and overlap. However, these contributions are not independent because of the equilibrium condition, and thus it is the overall fit which has meaning within his model, not the individual contributions.

This feature of model fitting to the elastic constants is evident from Eq. (8). The relation for C_{44} [Eq. (8d)] contains a term from the volume contribution. However, equilibrium at zero initial stress requires that C_1 in Eq. (8a) is zero, yielding a relation between the potential and the volume contribution. For fitting to experimental elastic constants, it is immaterial whether Eq. (8d) is used as given or is converted to

$$C_{44}=\frac{1}{2\Omega_0}\sum_s \psi_s''(x^s)^2(y^s)^2+\frac{1}{2\Omega_0}\sum_s \psi_s'(x^s)^2\ .$$

Although the corresponding relations are more complex in the Thomas model, the various contributions cannot be independent of each other.

A rough fit to the second-order elastic constants of Cu and Ag can be obtained with a one-parameter model, the parameter being the curvature of a two-body central potential between nearest neighbors (the slope of the potential taken as zero so that the lattice is in equilibrium with no additional forces). Any model which incorporates this parameter will yield approximate cancellation of the contributions from additional terms. The same holds true for the third-order elastic constants, the parameter

TABLE I. Least-squares fit to experimental data for the third-order elastic constant parameters for copper discussed in the text. All terms are given in 10^{12} dyn/cm^2.

		Experimental			Fitted				
	T (°K)	K_{100}	K_{110}	K_{111}	A	B	K_{100}	K_{110}	K_{111}
PB + P[a]	0	−15.1	−33.2	−28.7	−16.32	1.01	−15.3	−33.7	−28.0
PB + P[a]	300	−13.9	−31.2	−25.7	−15.34	1.47	−13.9	−31.1	−25.8
S + A[b]	0	−20.0	−35.3	−32.5	−14.02	−6.36	−20.4	−36.1	−31.3
S + A[b]	300	−15.0	−29.5	−27.2	−13.36	−2.07	−15.4	−30.5	−25.8
H + G[c]	300	−12.7	−32.7	−29.5	−18.32	5.14	−13.3	−34.0	−27.6

[a] See Ref. 12.

[b] See Ref. 11.

[c] See Ref. 7.

TABLE II. Lattice-model fit to the experimental elastic constants for copper. All terms are given in 10^{12} dyn/cm^2.

	T (°K)	C_{11}	C_{12}	C_{44}	K_{100}	K_{110}	K_{111}
Present	0	1.78	1.27	0.81	−14.8	−33.1	−27.5
Thomas[a]	0	1.79	1.26	0.83	−17.0	−36.5	−29.9
Overton and Gaffney[b]	0	1.76	1.25	0.82			
Peters *et al.*[c]	0				−15.1	−33.2	−28.7
Salama and Alers[d]	0				−20.0	−35.3	−31.6
Present	300	1.65	1.18	0.76	−13.7	−30.8	−25.6
Overton and Gaffney[b]	300	1.68	1.21	0.75			
Peters *et al.*[c]	300				−13.9	−31.2	−25.7
Salama and Alers[d]	300				−15.0	−29.5	−27.2
Hiki and Granato[e]	300				−12.7	−32.7	−29.4

[a] See Ref. 6.

[b] See Ref. 8.

[c] See Ref. 12.

[d] See Ref. 11.

[e] See Ref. 7.

being the third derivative of a nearest-neighbor two-body central potential. This rough fitting has been discussed by Hiki and Granato.[7]

Most point-defect calculations have been carried out for cubic metals in which a short-ranged two-body interatomic potential, together with some scheme to produce equilibrium, yields a satisfactory fit to the second-order elastic constants. The equations presented above can be simply applied to refine these empirical lattice-model potentials with respect to third derivatives.

ACKNOWLEDGMENT

It is a pleasure to acknowledge stimulating discussions with David Brudnoy during the course of this work.

APPENDIX

The second-order elastic constants for copper measured by Overton and Gaffney[8] and Rayne[9, 10] at 0 and 300 °K show excellent agreement. However, the third-order constants given by Hiki and Granato,[7] Salama and Alers,[11] and Peters, Breazeale, and Paré[12] contain significant discrepancies. Peters *et al.* only give three constants:

$$K_{100}=C_{111}\ ,$$

$$K_{110}=\tfrac{1}{4}(C_{111}+3C_{112}+12C_{166})\ ,$$

and

$$K_{111}=\tfrac{1}{9}(C_{111}+6C_{112}+24C_{166}+2C_{123}+12C_{144}+16C_{456}).$$

For a lattice model with a two-body nearest-neighbor central potential and a single volume-dependent term, these three constants are determined by two parameters:

$$K_{100}=A+B\ ,$$

$$K_{110}=\tfrac{17}{8}A+B\ ,$$

and

$$K_{111}=\tfrac{16}{9}A+B\ ,$$

with

$$A=(1/2\Omega_0)[a_1^3\phi_1'''-3a_1^2\phi_1''+3a_1\phi_1^1]$$

and

$$B=n(n-2)(n-4)P\ .$$

A least-squares fit to the experimental data is given in Table I. The parameter B shows little consistency, while the room-temperature data by Peters *et al.* give the best over-all agreement. Also, the value of B for this case is close to that predicted by an exact fit to the second-order constants. Thus the lattice model listed in the next paragraph was biased towards a fit to these data.

Generally good agreement was obtained with the following lattice model: $a_1^2\phi_1''=-13\tfrac{2}{3}a_1\phi_1^1$ ($13\tfrac{2}{3}$ corresponds to the common Born-Mayer exponential parameter), $a_1^3\phi_1'''=-12\tfrac{1}{2}a_1^2\phi_1''$, $n=\tfrac{1}{2}$, and the ratio

$$(1/\Omega_0)a_1^i\phi_1^i\,|_{0\,°\mathrm{K}}/(1/\Omega_0)a_1^i\phi_1^i\,|_{300\,°\mathrm{K}}$$

$$=1.075 \text{ for } i=1,\ 2,\ \text{and } 3\ .$$

With $(1/\Omega_0)a_1^2\phi_1''\,|_{0°\mathrm{K}}=2.08\times10^{12}$ dyn/cm^2, this model gives the values in Table II.

The primary reason the calculations by Thomas yield somewhat higher values for the third-order constants than the present fit is that he took

$$a_1^3\phi_1'''/a_1^2\phi_1''=a_1^2\phi_1''/a_1\phi_1^1\ ,$$

whereas the magnitude of the left-hand ratio was taken as slightly smaller than the right-hand ratio in the present model.

†Work supported by the United States Atomic Energy Commission under Contract No. AT-(40-1)-3108.

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